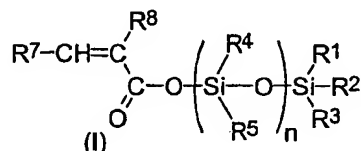


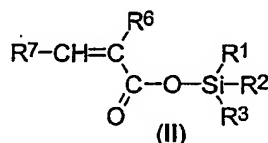
Claims

1. Process for the preparation of polyorganosilylated carboxylate monomers of general formula (I) or polymers thereof, comprising the steps of:



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reacting a cyclosiloxane of formula  $(\text{R}^4\text{R}^5\text{SiO})_n$  with unsaturated organosilylated carboxylate of formula (II) or copolymers thereof under the presence of a suitable catalyst,



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wherein  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$  each independently represent hydrogen, alkyl, alkenyl, alkynyl, alkyloxy, aryl, aralkyl or halogen radical optionally substituted by one or more substituents independently selected from the group comprising alkyl, aralkyl, aryl, hydroxy, halogen, amino or amino alkyl radicals,

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$\text{R}^6$  represents hydrogen, alkyl radical, or  $-\text{CH}_2\text{-CO}_2\text{-SiR}^1\text{R}^2\text{R}^3$ ,

$\text{R}^7$  represents hydrogen, alkyl radical or  $-\text{COOR}^9$  wherein

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$\text{R}^9$  represents an alkyl group,

$\text{R}^8$  represents hydrogen, alkyl radical or  $-\text{CH}_2\text{-CO}_2\text{-(SiR}^4\text{R}^5\text{O)}_n\text{-SiR}^1\text{R}^2\text{R}^3$ , and

$n$  represents a number of dihydrocarbylsiloxane units from 3 to 20.

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2. Process according to claim 1, wherein  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$ ,  $\text{R}^6$  and  $\text{R}^9$  are each independently selected from the group comprising methyl, ethyl, propyl, isopropyl, isobutyl, n-butyl, sec-butyl, t-butyl.

3. Process according to claim 2, wherein  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$  and  $R^9$  are methyl.
4. Process according to any of claims 1 to 3, wherein  $n$  represents a number of dihydrocarbylsiloxane units from  
5 3 to 12, preferably from 3 to 8, more preferably from 3 to 6.
5. Process according to claim 4, wherein  $n$  is 3.
6. Process according to any of claims 1 to 5, wherein said unsaturated organosilylated carboxylate of formula (II)  
10 is selected from the group comprising trimethylsilyl (meth)acrylate, tri-*t*-butylsilyl (meth)acrylate, tribenzylsilyl (meth)acrylate, triethylsilyl (meth)acrylate, tri-isopropylsilyl (meth)acrylate, tri-isobutylsilyl (meth)acrylate, tri-*n*-amylsilyl (meth)acrylate,  
15 (meth)acrylate, tri-*n*-butylsilyl (meth)acrylate, tri-*n*-dodecylsilyl (meth)acrylate, tri-*n*-hexylsilyl (meth)acrylate, tri-*n*-octylsilyl (meth)acrylate, tri-*n*-propylsilyl (meth)acrylate, triphenylsilyl (meth)acrylate, tri-*p*-methylphenylsilyl (meth)acrylate,  
20 dibutylcyclohexylsilyl (meth)acrylate, dibutylphenylsilyl (meth)acrylate; dicyclohexylphenylsilyl (meth)acrylate, diisopropyl-*n*-butylsilyl (meth)acrylate, diisopropylstearyl-silyl (meth)acrylate, dimethylbutylsilyl (meth)acrylate,  
25 dimethylcyclohexylsilyl (meth)acrylate, dimethylhexylsilyl (meth)acrylate, dimethyloctylsilyl (meth)acrylate, dimethylphenylsilyl (meth)acrylate, ethyldibutylsilyl (meth)acrylate, ethyldimethylsilyl (meth)acrylate, lauryldiphenylsilyl (meth)acrylate,  
30 methyldibutylsilyl (meth)acrylate, *n*-octyldi-*n*-butylsilyl (meth)acrylate, *t*-butyl dimethylsilyl (meth)acrylate *t*-butyldiphenylsilyl (meth)acrylate, bis(trimethylsilyl) itaconate, *t*-butyldiphenylsilyl

methyl fumarate, t-butyldiphenylsilyl methyl maleate, t-butyldiphenylsilyl n-butyl fumarate, t-butyldiphenylsilyl n-butyl maleate, triisopropylsilyl amyl fumarate, triisopropylsilyl amyl maleate, 5 triisopropylsilyl methyl fumarate, triisopropylsilyl methyl maleate, tri-n-butylsilyl n-butyl fumarate, tri-n-butylsilyl n-butyl maleate, and polymers or copolymers thereof and the like.

7. Process according to claim 6, wherein said unsaturated 10 organosilylated carboxylate of formula (II) is selected from the group comprising trimethylsilyl (meth)acrylate, tri-t-butylsilyl (meth)acrylate, tribenzylsilyl (meth)acrylate, triethylsilyl (meth)acrylate, tri-isopropylsilyl (meth)acrylate, tri- 15 isobutylsilyl (meth)acrylate, tri-n-amylsilyl (meth)acrylate, tri-n-butylsilyl (meth)acrylate, tri-n-dodecylsilyl (meth)acrylate, tri-n-hexylsilyl (meth)acrylate, tri-n-octylsilyl (meth)acrylate, tri-n-propylsilyl (meth)acrylate and triphenylsilyl 20 (meth)acrylate and polymers or copolymers thereof.

8. Process according to claim 7, wherein said unsaturated organosilylated carboxylate of formula (II) is trimethylsilyl methacrylate or a copolymer or a polymer thereof.

9. Process according to any of claims 1 to 8, wherein said 25 cyclosiloxane of formula  $(R^4R^5SiO)_n$  is selected from the group comprising 1,1,3,3,5,5-hexamethyl-cyclotrisiloxane (D3), 1,1,3,3,5,5-hexaethyl-cyclotrisiloxane, 1,1,3,3,5,5-hexaphenyl-cyclotrisiloxane, 1,1,3,3,5,5-hexavinyl-cyclotrisiloxane, 1,3,5-trimethyl-1,3,5-trivinyl-cyclotrisiloxane, 1,3,5-trimethyl-1,3,5-triphenyl-cyclotrisiloxane, 1,3,5-trimethyl-1,3,5-tripropyl-

cyclotrisiloxane, 1,3,5-triethyl-1,3,5-trimethyl-  
 cyclotrisiloxane, 1,3,5-trimethyl-1,3,5-triphenethyl-  
 cyclosiloxane, 1,3,5-trivinyltrihydro-cyclotrisiloxane,  
 1,3,5-trimethyltrihydro-cyclotrisiloxane, pentamethyl-  
 5 cyclotrisiloxanes, 1,1,3,3,5,5,7,7-octamethyl-  
 cyclotetrasiloxane (D4), 1,1,3,3,5,5,7,7-octaphenyl-  
 cyclotetrasiloxane, 1,1,3,3,5,5,7,7-octavinyl-  
 cyclotetrasiloxane, 1,1,3,3,5,5,7,7-octahydro-  
 cyclotetrasiloxane, 1,3,5,7-tetramethyl-1,3,5,7-  
 10 tetrahydro-cyclotetrasiloxane, 1,3,5,7-tetramethyl-  
 1,3,5,7-tetra(1-octyl)-cyclotetrasiloxane, 1,3,5,7-  
 tetravinyl-1,3,5,7-tetramethyl-cyclotetrasiloxane,  
 1,3,5,7-tetravinyl-1,3,5,7-tetraethyl-  
 cyclotetrasiloxane, 1,3,5,7-tetraallyl-1,3,5,7-  
 15 tetraphenyl-cyclotetrasiloxane, 1,3,5,7-tetra(1-  
 hexadecyl)-1,3,5,7-tetramethyl-cyclotetrasiloxane,  
 1,3,5,7-tetraoctyltetrahydro-cyclotetrasiloxane,  
 1,3,5,7-tetravinyltetrahydro-cyclotetrasiloxane,  
 1,3,5,7-tetraethyltetrahydro-cyclotetrasiloxane,  
 20 1,3,5,7-tetrapropenyltetrahydro-cyclotetrasiloxane,  
 1,3,5,7-tetrapentenyltetrapentyl-cyclotetrasiloxane;  
 1,3,5,7-tetraphenyltetrahydro-cyclotetrasiloxane,  
 pentamethyl-cyclotetrasiloxanes, hexamethyl-  
 cyclotetrasiloxanes, 1,1,3,3,5,5,7,7,9,9-decamethyl-  
 25 cyclopentasiloxane (D5), 1,1,3,3,5,5,7,7,9,9-decahydro-  
 cyclopentasiloxane, 1,3,5,7,9-pentavinyl-1,3,5,7,9-  
 pentamethyl-cyclopentasiloxane, 1,3,5,7,9-pentadecenyl-  
 1,3,5,7,9-pentapropyl-cyclopentasiloxane, 1,3,5,7,9-  
 pentamethylpentahydro-cyclopentasiloxane, 1,3,5,7,9-  
 30 pentavinylpentahydro-cyclopentasiloxane, tetramethyl-  
 cyclopentasiloxanes, hexamethyl-cyclopentasiloxanes,  
 heptamethyl-cyclopentasiloxanes,  
 1,1,3,3,5,5,7,7,9,9,11,11-dodecamethyl-

cyclohexasiloxane (D6), 1,1,3,3,5,5,7,7,9,9,11,11-dodecahydro-cyclohexasiloxane, 1,3,5,7,9,11-hexavinylhexamethyl-cyclohexasiloxane, 1,3,5,7,9,11-hexamethylhexahydro-cyclohexasiloxane, tetramethyl-cyclohexasiloxanes, pentamethyl-cyclohexasiloxanes, 1,3,5,7,9,11,13,15,17,19-decavinyldecahydro-cyclodecasiloxane, 1,3,5,7,9,11,13,15,17,19,21,23,25,27,29-pentadecavinylpentadecahydro-cyclopentadecasiloxane and the like..

10. Process according to claim 9, wherein said cyclosiloxane of formula  $(R^4R^5SiO)_n$  is selected from the group comprising 1,1,3,3,5,5-hexamethyl-cyclotrisiloxane (D3), 1,1,3,3,5,5,7,7-octamethyl-cyclotetrasiloxane (D4), 1,1,3,3,5,5,7,7,9,9-decamethyl-cyclopentasiloxane (D5), 1,1,3,3,5,5,7,7,9,9,11,11-dodecamethyl-cyclohexasiloxane (D6).

11. Process according to claim 10, wherein said cyclosiloxane of formula  $(R^4R^5SiO)_n$  is 1,1,3,3,5,5-hexamethyl-cyclotrisiloxane (D3).

12. Process according to any of claims 1 to 11, wherein said suitable catalyst for the reaction is an acidic catalyst.

13. Process according to claim 12, wherein said catalyst is selected from the group comprising hydrochloric acid, acetic acid, nitric acid, sulfuric acid, trifluoromethanesulfonic acid, trifluoroacetic acid, acetic acid, AMBERLYST A15, AMBERLYST 38 W, AMBERLYST 36, AMBERJET 1500H, AMBERJET 1200H, DOWEX MSC-1, DOWEX 50W, DELOXAN ASP I/9, DIAION SK1B, LEWATIT VP OC 1812, LEWATIT S 100 MB, LEWATIT S 100 G1, NAFION SAC13,

NAFION NR50, CT275,  $\text{ZnCl}_2$ ,  $\text{BeCl}_2$ ,  $\text{TiCl}_4$ ,  $\text{SnCl}_4$ ,  $\text{FeCl}_3$ ,  $\text{FeCl}_2$ ,  $\text{SbCl}_5$ ,  $\text{AlCl}_3$  and other metal halides.

14. Process according to claim 13, wherein said catalyst is  $\text{ZnCl}_2$ .

5 15. Process according to claim 13, wherein said catalyst is trifluoromethanesulfonic acid.

16. Process according to claim 13, wherein said catalyst is AMBERLYST A15.

10 17. Process according to any of claims 12 to 16, further comprising the steps of neutralising the acidic catalyst with a base.

18. Process according to claim 17, wherein said base is selected from the group comprising triethylamine, diethylamine, tributylamine, hexamethyldisilazane N-methylmorpholine,  
15 diisopropylethylamine, dicyclohexylamine, N-methylpiperidine, pyridine, 4-pyrrolidinopyridine, picoline, 4-(N,N-dimethylamino)pyridine, 2,6-di(t-butyl)-4-methylpyridine, quinoline, N,N-dimethylaniline and N,N-diethylaniline and the like.  
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19. Process according to claim 18, wherein said base is triethylamine.

20. Process according to any of claims 1 to 19, wherein the step of reacting the cyclosiloxane of formula  
25  $(\text{R}^4\text{R}^5\text{SiO})_n$  with the unsaturated organosilylated carboxylate of formula (II) or a copolymer or a polymer thereof is optionally performed in the presence of a suitable solvent.

21. Process according to claim 20, wherein said solvent is  
30 a nonpolar inert solvent selected from the group comprising benzene, toluene, xylene, mesitylene, ethylbenzene, pentane, hexane, cyclohexane, heptane, octane, decane, decahydronaphthalene, diethyl ether,

diisopropyl ether, diisopropyl ether, diisobutyl ether, or mixtures thereof.

22. Process according to any of claims 1 to 21, wherein said reaction is preformed at a temperature selected in the range of 20 to 150 °C, preferably 50 to 120 °C, more preferably 90 to 110 °C.

23. Process according to any of claims 1 to 22, wherein said reaction is performed at room temperature.

24. Polyorganosilylated carboxylate monomers of formula (I) or polymers thereof obtained by the process according to any of claims 1 to 23.

25. Polyorganosilylated carboxylate monomers of formula (I) or polymers thereof obtainable by the process according to any of claims 1 to 23.

26. Polyorganosilylated carboxylate monomers or polymers thereof according to any of claims 24 or 25, wherein  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$  and  $R^9$  are each independently selected from the group comprising methyl, ethyl, propyl, isopropyl, isobutyl, n-butyl, sec-butyl, t-butyl.

27. Polyorganosilylated carboxylate monomers or polymers thereof according to claim 26, wherein  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$  and  $R^9$  are methyl.

28. Polyorganosilylated carboxylate monomers or polymers thereof according to any of claims 24 to 27, wherein n represents a number of dihydrocarbylsiloxane units from 3 to 12, preferably from 3 to 8, more preferably from 3 to 6.

29. Polyorganosilylated carboxylate monomers or polymers thereof according to claim 28, wherein n is 3.

30. Use of a polyorganosilylated carboxylate monomers or polymers thereof according to any of claims 24 to 29 in coating compositions.

31. Use of polyorganosilylated carboxylate monomers according to any of claims 24 to 30 as comonomer unit in the binder of antifouling coating compositions.